



A triphenylamine based multi-analyte chemosensor for Hg²⁺ and Cu²⁺ ions in MeCN/H₂O



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ARTICLE INFO

Article history:

Received 20 April 2014

Received in revised form 20 June 2014

Accepted 26 June 2014

Available online 2 July 2014

Keywords:

Triphenylamine
Oxidative cyclization
Multianalyte sensor
Triazole
Radical cation

ABSTRACT

A novel triphenylamine based oxidative chemosensor **TOC** was synthesized. The chromogenic and fluorogenic behaviors of **TOC** towards Hg²⁺ and Cu²⁺ ions in a binary mixture of MeCN/H₂O (9/1) were dramatically different. **TOC** displays colorimetric 'naked eye' recognition of Hg²⁺ and fluorogenic 'turn on' response towards Cu²⁺ via a unique cyclization reaction using two different detection modes. Moreover, **TOCAZOL** obtained from the oxidative cyclization reaction of **TOC** with Cu(ClO₄)₂ can be used as a selective fluorescent sensor toward Hg²⁺ ion.

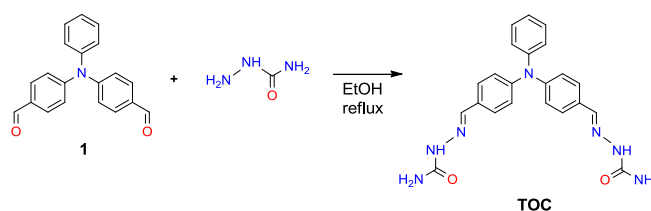
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1. Introduction

The design and synthesis of selective chemosensors for the detection of transition and heavy metal ions has been attracted considerable attention because they play essential roles in physiological and environmental processes.¹ Therefore, developing a simple and highly selective method to monitor metal ion levels is an important research area. A variety of methods for measuring metal ion concentrations have been used including atomic absorption/emission spectroscopy,^{2,3} inductively coupled plasma-mass spectroscopy (ICPMS),^{4,5} inductively coupled plasma-atomic emission spectrometry (ICP-AES),^{6,7} and voltammetry.^{8,9} Most of these methods demand expensive devices and are not appropriate for on site assays. Recently, great attention has been paid to the development of colorimetric and fluorescent chemosensors for the detection of mercury(II)¹⁰ and copper(II)¹¹ ions because they offer several advantages over other analytical methods from the point of high sensitivity, high selectivity, fast response times, which can be used for real time monitoring, as well as nondestructive detection.

Triphenylamine (TPA) is three-armed fluorescent probe and structurally rigid. Although the quantum yield of TPA itself is not high, high quantum yield is achieved by peripheral functionalization.^{12,13} Only a few studies on TPA-based chemosensors have been published.¹⁴ Recently, we reported a turn-on fluorescent sensor

based on TPA for Zn²⁺ and Cd²⁺ ions in MeCN.¹⁵ The findings promote us to design a novel TPA-based metal ion sensor. The synthetic route to receptor **TOC** (Triphenylamine Oxidative Chemosensor) is outlined in Scheme 1.



Scheme 1. Synthesis of triphenylamine semicarbazone receptor.

2. Results and discussion

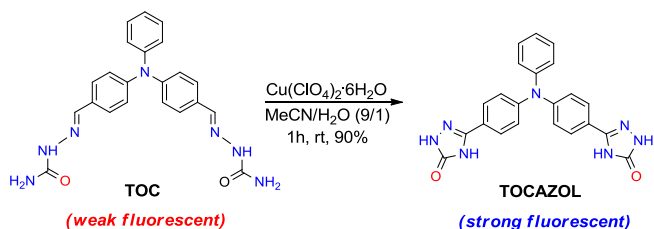
2.1. Synthesis and characterization

Triphenylamine dialdehyde (**1**) was easily converted to semicarbazone derivate by refluxing **1** with semicarbazide hydrochloride in ethanol. The chemical structures of the synthesized compounds have been confirmed by the combination of ¹H NMR, ¹³C NMR, APT, COSY, FTIR spectra, and elemental analysis (Supplementary data). The infrared spectrum of **TOC** shows the bands in the region of 3464–3311 cm⁻¹ are due to the asymmetric and symmetric –NH₂ stretching frequencies while NH vibration is

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present at 3182 cm^{-1} . The typical bands of the aliphatic CH of **TOC** appear in the range of $3032\text{--}2979\text{ cm}^{-1}$. The strong bands at 1670 and 1582 cm^{-1} can be assigned to C=O and C=N vibrations, respectively. The C=C vibrations of the phenyl group of **TOC** are observed in the region of $1581\text{--}1561\text{ cm}^{-1}$. **TOC** may exist in keto-enol tautomerization, however, the absence of any bands corresponding to enol group reveals the presence of only the keto tautomer of **TOC** in the solid state.

In the ^1H NMR spectrum of **TOC**, the signals of the N–H proton are observed as singlet at δ 10.20 while NH_2 protons produce a broad singlet at δ 6.45. All these protons disappear after exchange with D_2O . The azomethine signal of **TOC** appears as a singlet at δ 7.79. The signals of the aromatic protons of the **TOC** are observed at δ 7.71–6.98 and their integrations are consistent with the assigned structures. The proton decoupled ^{13}C spectrum of the compound contains 10 peaks corresponding to 10 sets of carbon atoms. As well as ^1H NMR, ^{13}C NMR, and FTIR analysis, the structure of receptors is supported by the combination of APT and COSY NMR spectra (Supplementary data) (Scheme 2).



Scheme 2. Conversion of triphenylamine semicarbazone to 1,4-dihydro-1,2,4-triazol-5-one derivative.

2.2. UV–vis and fluorescence studies

Aqueous media are essential for monitoring environmental, biological, and industrial samples. The emission intensity of **TOC** gradually decreased corresponding to the increase of the water content, and maximum quenching was observed when the water content reaches about 10% (v/v) (Supplementary data, Fig. S1). Therefore, UV–vis and fluorescence probing experiments were performed in a binary mixture of MeCN/ H_2O (9/1).

To probe the sensing ability of receptors, a wide range of metal ions (Li^+ , Na^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ag^+ , Zn^{2+} , Cd^{2+} , Hg^{2+} , Al^{3+} , and Pb^{2+}) were tested by UV–vis spectroscopy in MeCN/ H_2O (9/1) at room temperature (Fig. 1). In the absence of any metal ion, **TOC** exhibits three absorptions. The absorption band around 271 and 340 nm was

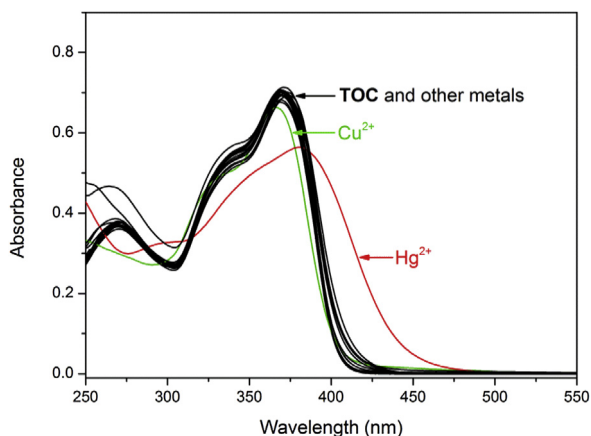


Fig. 1. UV–vis spectra of **TOC** ($20.0\text{ }\mu\text{M}$) in the presence of 5.0 equiv of various metal ions in a solution of MeCN/ H_2O (9/1).

assigned to a $\pi\text{--}\pi^*$ transitions in triphenylamine, third absorption band around 370 nm attributed to $n\text{--}\pi^*$ transitions in imine linkages. Addition of 5.0 equiv of test metal ions to the solutions of **TOC** caused no significant change in absorption, except for Hg^{2+} . The visual color change from colorless to yellow upon addition of Hg^{2+} is easily perceptible to the naked eye for **TOC**. Meanwhile, the addition of Cu^{2+} to **TOC** barely influences the absorption spectrum. Thus, **TOC** can serve as a selective colorimetric sensor for Hg^{2+} (Supplementary data, Fig. S2).

To determine the stoichiometry of receptor, the mole-ratio method was used. The titration profile (Fig. 2) clearly indicates a 1:1 stoichiometric ratio for **TOC**– Hg^{2+} . The logarithmic stability constant, K_s of **TOC**– Hg^{2+} , was calculated as 6.02 M^{-1} on the basis of Harvey and Manning method¹⁶ using the mole-ratio data. The results showed that hard–soft compatibility is the key to monitor sensitivity and selectivity in the presence of other metal ions. According to Pearson's hard–soft acid–base theory,¹⁷ soft sulfur or nitrogen centers may be the best choice for the selective recognition of soft Hg^{2+} and borderline Cu^{2+} ions. A key structural feature of these fascinating receptors consists of their mixed donor atoms of N,O influencing sensing properties. These combinations provide multi-analyte sensing ability.

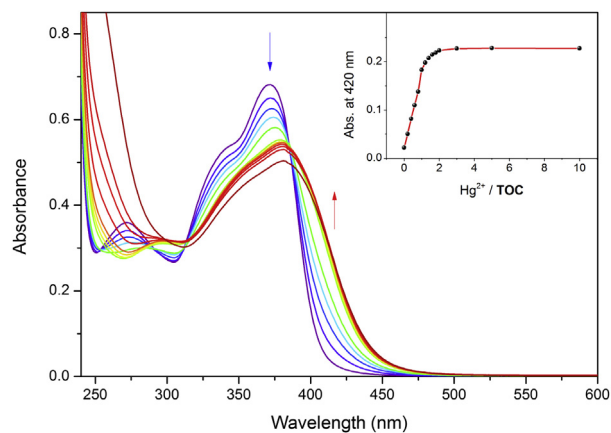


Fig. 2. UV–vis titration of **TOC** ($20.0\text{ }\mu\text{M}$) with the addition of increasing concentration of Hg^{2+} (10.0 mM) in MeCN/ H_2O (9/1). Inset: mole-ratio plot for interaction of **TOC** with Hg^{2+} at 420 nm.

The detection limit of **TOC**– Hg^{2+} is calculated as $2.39\text{ }\mu\text{M}$ based on UV–vis titration data. The values for the metal ions studied are measured to be less than 3 ppm. This result shows that **TOC** possesses a high sensitivity in detecting Hg^{2+} ions in a binary mixture MeCN/ H_2O (9/1).

The fluorescence response of **TOC** towards the studied metal ions was investigated (Fig. 3). Addition of Cu^{2+} led to a significant enhancement in the emission of **TOC**. Only Hg^{2+} ion showed a slight quenching effect. Other tested metal ions have no or very little effect on the emission. Interestingly, it was observed that the emission intensity of **TOC** after the addition of Cu^{2+} has been considerably increased in the process of time. The quenching by Hg^{2+} ion is most likely due to an energy transfer having occurred from electron donor part of receptor to the bound metal ion centers showing a faster and more efficient nonradiative decay of the excited states. However, the enhanced fluorescence upon addition of Cu^{2+} to **TOC** in MeCN/ H_2O (9/1) is due to the formation of a novel 1,4-dihydro-1,2,4-triazol-5-one derivative (**TOCAZOL**) through the oxidative cyclization of semicarbazone moieties (Scheme 2).

To understand the effect of other tested metal ions on the interaction of Cu^{2+} with **TOC**, competitive experiments were conducted in the presence of Cu^{2+} ($5.0\text{ }\mu\text{M}$) and other metal ions ($5.0\text{ }\mu\text{M}$) (Fig. 4). The results showed that emission enhancement

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